# PATENT ABSTRACTS OF JAPAN

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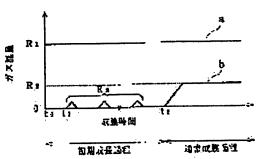
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### (54) MANUFACTURE OF SEMICONDUCTOR DEVICE

(57)Abstract:

PROBLEM TO BE SOLVED: To enable forming a nitride film having high resistance to leak and excellent characteristics even if the film thickness is small, by intermittently supplying a constant amount of silicon containing gas while continuously supplying ammonia gas, and then continuously supplying a constant amount of silicon containing gas.

SOLUTION: When a silicon nitride film is formed on a semiconductor substrate, silicon containing gas (b) is intermittently supplied to the inside of a film forming equipment accommodating the semiconductor substrate, while continuously supply a constant amount R1 of ammonia gas (a). After that, a constant amount R2 of silicon containing gas (b) is continuously supplied to the inside of the film forming equipment, while supplying the constant amount R1 of the ammonia gas (a). For example, NH3 with a flow rate of 750ccm is supplied, and then SiH2Cl2 of 0.5cc is supplied at a time t1. The period of intermittent supply is set to be 20 seconds,



and SiH2Cl2 is supplied about 20 times. After that, from a time t2, SiH2Cl2 with a flow rate of 50ccm is continuously supplied for about 4-5 minutes, thereby forming a silicon nitride film.

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#### **CLAIMS**

[Claim(s)]

[Claim 1] Supplying the ammonia gas of a constant rate continuously in the membrane formation equipment which held said semi-conductor substrate in forming a silicon nitride on a semi-conductor substrate The 1st process which supplies intermittently the silicon content gas which contains silicon as a constituent, The manufacture approach of the semiconductor device characterized by having the 2nd process which supplies said silicon content gas of a constant rate continuously, supplying the ammonia gas of said constant rate continuously after said 1st process and in said membrane formation equipment.

[Claim 2] The manufacture approach of the semiconductor device according to claim 1 by which it is thing characterized with less amount of supply of said silicon content gas intermittently supplied in said 1st process than the amount of supply of said silicon content gas continuously supplied in said 2nd process.

[Claim 3] The manufacture approach of a semiconductor device according to claim 1 or 2 that said silicon content gas is characterized by being gas of a mono silane and dichlorosilane which contains either at least.

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### **DETAILED DESCRIPTION**

[Detailed Description of the Invention]

[0001]

[Field of the Invention] Especially this invention relates to the formation approach of the silicon nitride in a semiconductor device about the manufacture approach of a semiconductor device.

[Description of the Prior Art] Conventionally, the silicon nitride formed by reduced pressure chemistry vapor phase reaction has been used as one of the components of capacity insulator layers, such as DRAM. There is the approach of forming membranes with reduced pressure chemistry vapor phase reaction as the growth approach of a silicon nitride by making a mono silane (SiH4) or dichlorosilane (SiH2 Cl2), and ammonia (NH3) into material gas. At this time, it is SiH4 which is material gas conventionally. Or SiH2 Cl2 NH3 is always continuously supplied by the fixed flow rate from membrane formation initiation of a silicon nitride to termination.

[Problem(s) to be Solved by the Invention] In recent years, thickness of capacity insulator layers, such as DRAM, must also be inevitably made thin with detailed-izing of a semiconductor device. However, if the thickness is made thin, problems, such as an increment in leakage current and an oxidation-resistant fall, will produce a silicon nitride. If silicon becomes [ the presentation of the film ] superfluous rather than stoichiometry (Si:N=3:4), since membraneous quality -- oxidation resistance worsens -- will generally deteriorate in a silicon nitride, it becomes difficult to obtain a required capacity. On the other hand, the growth is unstable in order to grow up a silicon nitride on the film of different species, such as a polycrystal silicone film, in the initial stage of film growth. Therefore, in the formation approach of the conventional silicon nitride, it is the initial stage of membrane formation, and is SiH4 of the material gas. Or SiH2 Cl2 Membrane formation advanced only by decomposition and the inclination for the nucleus of a silicon nitride with little nitrogen with much silicon to grow compared with stoichiometry was seen. Therefore, the inclination of especially degradation of the membraneous quality of a silicon nitride was so remarkable that the last thickness became thin

[0004] Then, the purpose of this invention is offering the manufacture approach of a semiconductor device thickness's being able to form the nitride of a good property with high leak-proof nature as it is thin, even if.

[0005]

[Means for Solving the Problem] The manufacture approach of the semiconductor device of this invention which solves the technical problem mentioned above Supplying the ammonia gas of a constant rate continuously in the membrane formation equipment which held said semi-conductor substrate in forming a silicon nitride on a semi-conductor substrate It has the 1st process which supplies intermittently the silicon content gas which contains silicon as a constituent, and the 2nd process which supplies said silicon content gas of a constant rate continuously while supplying the ammonia gas of said constant rate continuously after said 1st process and in said membrane formation equipment.

[0006] In one mode of this invention, there is less amount of supply of said silicon content gas intermittently supplied in said 1st process than the amount of supply of said silicon content gas continuously supplied in said 2nd process.

[0007] In one mode of this invention, said silicon content gas is gas of a mono silane and dichlorosilane which contains either at least.

[Embodiment of the Invention] Hereafter, with reference to <u>drawing 1</u>, this invention is explained according to the gestalt of the desirable operation.

[0009] <u>Drawing 1</u> shows change of each quantity of gas flow of NH3 (inside a of drawing) and SiH2 Cl2 (inside b of drawing) in the formation approach of the silicon nitride by 1 operation gestalt of this invention, an axis of abscissa shows time amount and an axis of ordinate shows a quantity of gas flow. here -- time of day t0 from -- t2 up to -- an initial growth process and time of day t2 Henceforth is usually called a membrane formation process.

[0010] First, an initial growth process is explained. The semi-conductor substrate which should form a silicon nitride is held in membrane formation equipment, and it is the time of day t0 of <a href="mailto:drawing1">drawing1</a> NH3 Supply is started by flow rate 750ccm (R>1 <a href="drawing1">drawing1</a> R1). Henceforth, membrane formation temperature controls 750 degrees C, a pressure controls displacement, and it fixes to 0.5 Torr(s). time of day t0 from -- t1 \*\*\*\*\*\* -- NH3 Since it is supplied, a silicon nitride does not grow. Next, time of day t1 It sets and is SiH2 Cl2. 0.5 cc is supplied. This SiH2 Cl2 NH3 already supplied It reacts and a silicon nitride is grown up on a substrate. At this time, it is NH3. SiH2 Cl2 It compares, when supplying continuously by the respectively fixed flow rate. NH3 It is SiH2 Cl2 to the fixed inside which is carrying out flow rate supply. The direction supplied intermittently is NH3 per unit time amount. SiH2Cl2 It adds to a volume ratio becoming large. The grown-up silicon nitride is SiH2 Cl2 next. It is NH<SUB>3 until it is supplied. Since it is put and a part with superfluous silicon is nitrided certainly, the silicon nitride more near stoichiometry grows. And SiH2 Cl2 It is SiH2 Cl2 about 20 times, using the period of intermittent supply as 20 seconds. About 3-4A of silicon nitrides with a presentation ratio almost equal to stoichiometry is formed in (R3 of <a href="mailto:drawing1">drawing1</a>), and a substrate front face by supplying.

[0011] Next, a membrane formation process is usually explained. if a substrate front face is covered with a silicon nitride -- time of day t2 from -- SiH2 Cl2 during about 4 - 5 minutes It supplies continuously by the flow rate (R2 of drawing 1) of 50ccm(s), and the silicon nitride of the target thickness is grown up. Although these membrane formation [ in / usually / a membrane formation process ] conditions are equivalent to the membrane formation conditions of the silicon nitride by the conventional approach With the gestalt of this operation, since the substrate film formed by the initial growth process is a silicon nitride of a presentation of a chemistry theory ratio mostly Usually, the silicon nitride which has a presentation ratio almost equal to stoichiometry also in a membrane formation process grows, and the silicon nitride of the about 50-60A thickness which has a presentation ratio almost equal to stoichiometry as a result is formed.

[0012] thus, the time of the silicon nitride membrane formation near the interface with a substrate -- intermittent -- little by little -- SiH2 Cl2 supplying -- after that -- SiH2 Cl2 increasing the amount of supply and supplying continuously as usual -- up to membrane formation termination -- always -- intermittent -- SiH2 Cl2 the case where it supplies -- comparing -- a short time -- and a silicon nitride can be formed, without degrading membraneous quality.

[0013] In addition, it sets for an above-mentioned example and is SiH2 Cl2 in an initial growth process. If the intermittent amount of supply is changed, the optimal intermittent supply period will change according to it. Thus, the membrane formation temperature in an initial growth process and NH3 A flow rate, a pressure, and SiH2 Cl2 Since the membrane formation conditions in a membrane formation process have membrane formation conditions, such as an amount, a period, etc. of intermittent supply, and a different optimum value according to change of each item of the class of membrane formation equipment, or membrane formation conditions, values other than the value shown in the above-mentioned example can usually be taken.

[0014] Moreover, it is SiH2 Cl2 as silicon content gas which contains silicon in an above-mentioned example. Other gas 4 which contains silicon although used, for example, SiH, Even if it uses, it is almost the same.

[0015] Furthermore, in many cases, such as being formed on the capacitor lower electrode of a DRAM memory cell, a silicon nitride is formed on the semi-conductor substrate with which a certain extent component structure was formed, for example, although component structure may be directly

formed on the semi-conductor substrate which is not yet formed. Therefore, the word called "semi-conductor substrate" is used for mind also including the semi-conductor substrate with which a certain extent component structure was formed in this invention.

[0016] As explained above, the nuclear growth of a silicon nitride with superfluous silicon which becomes leakage current and the cause of oxidation-resistant degradation according to this invention is prevented, and it becomes possible to form the silicon nitride suitable for a chemistry theory ratio, and a required capacity can be secured with the semiconductor device made detailed.

[Effect of the Invention] According to this invention, even if, thickness can form the silicon nitride of a presentation ratio almost equal to stoichiometry with high oxidation resistance as it is thin, and a required capacity can be secured with the semiconductor device with which detailed-ization progresses.

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### DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

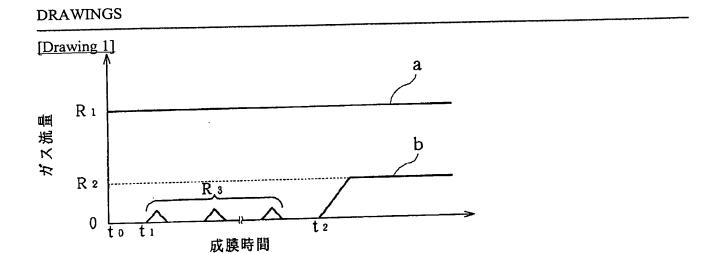
[Drawing 1] It is the graph which shows change of the quantity of gas flow by 1 operation gestalt of this invention.

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初期成長過程

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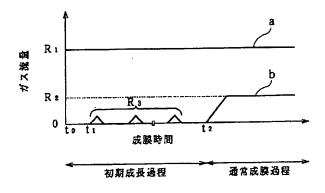
#### (54) 【発明の名称】 半導体装置の製造方法

#### (57)【要約】

【課題】たとえ膜圧が薄くとも、耐リーク性が高く、良好な特性のシリコン窒化膜を形成する。

【解決手段】一定量の $NH_3$  (a) を連続的に供給しながら、 $SiH_2$   $Cl_2$  又は $SiH_4$  (b) を間欠的に供給する初期成長過程と、一定量の $NH_3$  (a) を連続的に供給しながら、一定量の $SiH_2$   $Cl_2$  又は $SiH_4$ 

(b) を連続的に供給する通常成膜過程とを備える。



【特許請求の範囲】

【請求項1】 半導体基板上にシリコン窒化膜を形成するに当たり、

前記半導体基板を収容した成膜装置内に、一定量のアンモニアガスを連続的に供給しながら、珪素を構成成分として含む硅素含有ガスを間欠的に供給する第1の工程と、

前記第1の工程後、前記成膜装置内に、前記一定量のアンモニアガスを連続的に供給しながら、一定量の前記珪素含有ガスを連続的に供給する第2の工程とを有するこ 10とを特徴とする半導体装置の製造方法。

【請求項2】 前記第1の工程において間欠的に供給する前記珪素含有ガスの供給量が、前記第2の工程において連続的に供給する前記珪素含有ガスの供給量よりも少ないこと特徴とする請求項1に記載の半導体装置の製造方法。

【請求項3】 前記珪素含有ガスが、モノシラン及びジクロロシランの少なくともいずれかを含むガスであることを特徴とする請求項1又は2に記載の半導体装置の製造方法。

【発明の詳細な説明】

[0001]

【発明の属する技術分野】本発明は半導体装置の製造方法に関し、特に、半導体装置におけるシリコン窒化膜の 形成方法に関するものである。

[0002]

【従来の技術】従来、減圧化学気相反応法により成膜されたシリコン窒化膜はDRAM等の容量絶縁膜の構成要素の1つとして用いられてきた。シリコン窒化膜の成長方法としては、モノシラン(SiH4)或いはジクロロ 30シラン(SiH2 C12)とアンモニア(NH3)を原料ガスとして減圧化学気相反応法により成膜する方法がある。この時、従来は、原料ガスであるSiH4 或いはSiH2 C12 とNH3は、シリコン窒化膜の成膜開始から終了まで常に一定の流量で連続して供給される。

[0003]

【発明が解決しようとする課題】近年、半導体装置の微細化に伴い、DRAM等の容量絶縁膜の膜厚も必然的に薄くしなければならなくなってきた。しかし、シリコン窒化膜は、その膜厚を薄くしていくと、リーク電流の増加、耐酸化性の低下等の問題が生じてくる。一般に、シリコン窒化膜においては、その膜の組成が、化学量論比(Si:N=3:4)よりもシリコンが過剰になると、耐酸化性が悪くなる等、膜質が劣化するために、必要な容量を得ることが難しくなる。一方、膜成長の初期段階では、多結晶シリコン膜等の異種類の膜の上にシリコン窒化膜を成長させるため、その成長が不安定である。そのため、従来のシリコン窒化膜の形成方法においては、成膜の初期段階で、原料ガスのうちのSiH4或いはSiH2Cl2の分解のみで成膜が進行してしまい、化学50

最論比に比べてシリコンが多く窒素が少ないシリコン窒 化膜の核が成長する傾向が見られた。従って、シリコン 窒化膜の膜質の劣化は、特に、その最終膜厚が薄くなる ほどその傾向が顕著であった。

【0004】そこで、本発明の目的は、たとえ膜厚が薄くとも、耐リーク性の高い、良好な特性の窒化膜を形成することができる半導体装置の製造方法を提供することである。

[0005]

【課題を解決するための手段】上述した課題を解決する本発明の半導体装置の製造方法は、半導体基板上にシリコン窒化膜を形成するに当たり、前記半導体基板を収容した成膜装置内に、一定量のアンモニアガスを連続的に供給しながら、珪素を構成成分として含む硅素含有ガスを間欠的に供給する第1の工程と、前記第1の工程後、前記成膜装置内に、前記一定量のアンモニアガスを連続的に供給しながら、一定量の前記珪素含有ガスを連続的に供給する第2の工程とを有する。

【0006】本発明の一態様では、前記第1の工程において間欠的に供給する前記珪素含有ガスの供給量が、前記第2の工程において連続的に供給する前記珪素含有ガスの供給量よりも少ない。

【0007】本発明の一態様では、前記珪素含有ガスが、モノシラン及びジクロロシランの少なくともいずれかを含むガスである。

[0008]

【発明の実施の形態】以下、図1を参照して本発明をその好ましい実施の形態に従い説明する。

【0009】図1は、本発明の一実施形態によるシリコン室化膜の形成方法におけるNH3(図中a)とSiH2Cl2(図中b)の夫々のガス流量の変化を示しており、横軸は時間、縦軸はガス流量を示す。ここで、時刻toからt2までを初期成長過程、時刻t2以降を通常成膜過程と呼ぶ。

【0010】まず、初期成長過程について説明する。シ リコン窒化膜を成膜すべき半導体基板を成膜装置内に収 容し、図1の時刻 to に、NH3 流量750ccm(図 1のR1) で供給を開始する。以降、成膜温度は750 ℃、圧力は排気量を制御し0.5Torrに固定する。時刻 to からti までは、NH3 のみが供給されているので シリコン窒化膜は成長しない。次に、時刻 t 1 におい て、SiH2 Cl2 を0.5cc供給する。このSiH 2 C 12 は、既に供給されているNH3 と反応し基板上 にシリコン窒化膜を成長させる。この時、NH3 とSi H<sub>2</sub> C l<sub>2</sub> を夫々一定の流量で連続的に供給する場合に 比較して、NH3を一定の流量供給している中にSiH 2 Cl2 を間欠的に供給した方が単位時間当りのNH3 とSiH2Cl2の体積比は大きくなることに加え、成 長したシリコン窒化膜が、次にSiH2Cl2が供給さ れるまでの間、NH3 に曝され、シリコン過剰な部分が

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確実に窒化されるため、より化学量論比に近いシリコン窒化膜が成長する。そして、 $SiH_2CI_2$ の間欠供給の周期を20秒として20回程度 $SiH_2CI_2$ を供給することにより(図1の $R_3$ )、基板表面には殆ど化学量論比と等しい組成比を持つシリコン窒化膜が $3\sim4$  程度形成される。

【0011】次に、通常成膜過程について説明する。基板表面がシリコン室化膜に覆われたら、時刻  $t_2$  から約  $4\sim5$ 分間 $SiH_2$   $Cl_2$   $を50ccmの流量(図1のR_2)$  で連続的に供給し、目的の膜厚のシリコン窒化膜を成長させる。この通常成膜過程における成膜条件は、従来の方法によるシリコン窒化膜の成膜条件と同等であるが、本実施の形態では、初期成長過程で形成された下地膜がほぼ化学論比の組成のシリコン窒化膜であるために、通常成膜過程においても化学量論比とほぼ等しい組成比を持つシリコン窒化膜が成長し、結果として、化学量論比とほぼ等しい組成比を持つ50~60A程度の膜厚のシリコン窒化膜が形成される。

【0012】このように、基板との界面近傍のシリコン窒化膜成膜時にのみ間欠的に少しずつ $SiH_2Cl_2$ 供給し、その後は、 $SiH_2Cl_2$ の供給量を増加して従来通り連続的に供給することにより、成膜終了まで常に間欠的に $SiH_2Cl_2$ を供給する場合に比し、短時間で且つ膜質を劣化させることなくシリコン窒化膜を形成することができる。

【0013】なお、上述の例において、初期成長過程でのSiH2Cl2の間欠供給量を変えると、それに応じて、最適な間欠供給周期が変わる。このように、初期成長過程での成膜温度、NH3流量、圧力、SiH2Cl

2 の間欠供給の量と周期等の成膜条件や通常成膜過程での成膜条件は、成膜装置の種類や成膜条件の各項目の変化に応じて異なる最適値を有するために、上述の例で示した値以外の値を取り得る。

【0014】また、上述の例では、硅素を含む硅素含有ガスとして $SiH_2Cl_2$ 用いたが、珪素を含む他のガス、例えば、 $SiH_4$ を用いても殆ど同様である。

【0015】更に、シリコン窒化膜は、素子構造が未だ形成されていない半導体基板の上に直接形成される場合もあるが、例えば、DRAMメモリセルのキャパシタ下部電極の上に形成される等、多くの場合には、或る程度素子構造の形成された半導体基板の上に形成される。従って、本発明において、「半導体基板」と言う語は、或る程度素子構造の形成された半導体基板をも含めた意に用いる。

【0016】以上に説明したように、本発明によれば、 リーク電流や耐酸化性の劣化の原因となるシリコン過剰 なシリコン窒化膜の核成長を防ぎ、化学論比に合ったシ リコン窒化膜を形成することが可能になり、微細化した 半導体装置で必要な容量を確保できる。

#### [0017]

【発明の効果】本発明によれば、たとえ膜厚が薄くとも、耐酸化性の高い、化学量論比とほぼ等しい組成比のシリコン窒化膜を形成することができ、微細化が進む半導体装置で必要な容量を確保することができる。

#### 【図面の簡単な説明】

【図1】本発明の一実施形態によるガス流量の変化を示すグラフである。

